On confinement resonances in $A@C_{60}$ photoionization: easy to observe?

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(Dated: March 23, 2010)

Possible reasons that confinement resonances are not observed in a recent photoionization experiment on the endohedral fullerene $Ce@C_{82}^{+}$ are explored. The effect of the polarization of the fullerene shell in response to the ionization of the endohedrally encaged atom $A@C_n$, termed the "shielding" effect, has been investigated and found to be relatively small; no more than a 20% effect near threshold, and much less at higher energies. It is argued that most likely, the absence of confinement resonances in $Ce@C_{82}^{+}$ is due primarily to the finite thickness of the carbon cage; the off-the-center position and thermal vibration of the encaged atom, discussed elsewhere, further weaken the resonances rendering them beyond the sensitivity of the experiment to detect, in this case. For other situations/endohedrals, the confinement resonances should well be observable, and $Ne@C_{60}$ is suggested as an excellent candidate.

Photoionization spectra of atoms A encapsulated inside hollow fullerene cages C_n, referred to as endohedral atoms $A@C_n$, have been the subject of extensive theoretical study by a number of investigators at various levels of approximation for about a decade or so. The significance of these studies is that they provide information on how confinement changes properties of atoms. This information, in turn, is of considerable importance to basic science, as well as to applied sciences and technologies, since confined atoms are of multidisciplinary significance, see, e.g., Ref. [1].

An outstanding feature of the photoionization spectrum of the endohedral atom $A@C_n$ is associated with predicted resonances, termed confinement resonances, in the spectrum that have been extensively studied theoretically to date. The resonances occur due to the interference of the photoelectron waves emerging directly from the encapsulated (confined) atom A and those scattered off the C_n confining cage [2–8]. Note that oscillations of the similar nature have been seen, both theoretically and experimentally, in the photoionization of the free C_{60} fullerene where the photoelectron emerges from the C_{60} itself [9]. This phenomenology provides strong supporting evidence for the predicted existence of confinement resonances arising from the photoionization of the encaged atom in $A@C_{60}$ as well.

It has been not until very recently that a reliable experiment on the photoionization spectrum of an endohedral atom $A@C_n$ has become possible [10]. There, the $4d$ photoabsorption spectrum of Ce in $Ce@C_{82}^{+}$ has been experimentally measured. Aside from a very intriguing and still unresolved discovery of a significant redistribution of Ce $4d$ oscillator strengths in $Ce@C_{82}^{+}$ compared to free Ce, another finding was that no confinement res-

onances were observed in the spectrum, in contrast to expectations. Such expectations were primarily driven by theoretical results [11] where very strong confinement resonances in the $4d$ photoionization spectrum of Xe in $Xe@C_{60}$ were predicted. Note, in all cited theoretical studies associated with confinement resonances, including Ref. [11] on $Xe@C_{60}$, the encapsulated atom was positioned at the center of the cage.

The experimental data on $Ce@C_{82}^{+}$, on the one hand, challenge one to explain the absence of traces of confinement resonances in the $Ce@C_{82}^{+}$ spectrum. A suggested reason for this is associated with the off-the-center position of Ce in $Ce@C_{82}^{+}$ [4, 12] along with its thermal vibrations [4]. In the present paper, however, it is pointed out that confinement resonances in the $4d$ absorption spectrum of $Ce@C_{82}^{+}$ could hardly be observable even if the Ce atom were at the center of the cage, i.e., even omitting the off-the-center and thermal vibrations effects. On the other hand, the experiment poses a more troubling question, namely, whether some effects have been overlooked in the original theoretical predictions of confinement resonances that might "wash out" the resonances in the photoionization of an *at-the-center* encapsulated atom A in a C_n fullerene.

In any of earlier theoretical work on confinement resonances, the "shielding" effect was not considered in detail. The quintessence of the shielding effect is that while an outgoing photoelectron is passing through the C_n's wall, it could be partially or totally shielded from the Coulomb field of the final-state ion A^{+} when it is between the inner and outer surfaces of the carbon cage. This is because the final-state ion A^{+} can polarize the fullerene cage similar to a conducting shell. The electric potential of the central A^{+} is totally or partially canceled out by the electrostatic potential of an induced negative charge on the inner surface of C_n, thereby changing the potential experienced by the photoelectron while it is between the inner and outer surfaces of the C_n. The effect of total cancelation will occur if the cage acts as a perfect

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conductor. A partial cancelation will ensue if the cage is only somewhat polarizable. The impact of the shielding effect on confinement resonances is detailed below.

Following our earlier work [2, 7, 8], a spherical C_n cage will be modeled by a short-range, spherical potential $U_c(r)$ of the inner radius r_0, thickness Δ, and depth U_0:

$$U_c(r) = \begin{cases} U_0 < 0, & \text{if } r_0 \leq r \leq r_0 + \Delta \\ 0 & \text{otherwise.} \end{cases} \quad (1)$$

For C_{60}, $r_0 = 5.8$ a.u., $\Delta = 1.9$ a.u., and $U_0 = -8.2$ eV [2, 7, 8]. The applicability of the model is generally limited to low photoelectron energies when the photoelectron wavelength significantly exceeds the bond length between the carbon atoms of C_n, so that the C_n cage "looks" as a homogeneous charge distribution to the outgoing photoelectron. This potential is added to the atomic Hartree-Fock Hamiltonian $\hat{H}_0^{HF}$ (which is defined in the manner of an isolated atom) thereby forming a "confined" HF Hamiltonian

$$\hat{H}_c = \hat{H}_0^{HF} + U(r). \quad (2)$$

Solutions of the corresponding "confined" HF equation $\hat{H}_c \psi_i(\mathbf{r}) = E_i \psi_i(\mathbf{r})$ give one the initial ground-state electronic energies E_i as well as both the ground-state $\psi_i(\mathbf{r})$ and final-state $\psi_f(\mathbf{r})$ wavefunctions. This is how the energies and wavefunctions of a confined atom were defined originally [2, 7, 8].

To account for the shielding effect on an outgoing photoelectron while it is passing through the C_n, we introduce a re-defined final-state "confined" Hamiltonian $\hat{\mathcal{H}}_c$ which replaces $\hat{H}_c$ in the HF equation,

$$\hat{\mathcal{H}}_c = \begin{cases} \hat{H}_c - \frac{\alpha}{r}, & \text{if } r_0 \leq r \leq r_0 + \Delta \\ \hat{H}_c, & \text{otherwise.} \end{cases} \quad (3)$$

Here, $\alpha = 0$ if the shielding effect is ignored, as in earlier studies, $\alpha = 1$ for complete shielding of the ion-core potential of the final-state ion A^+ by the polarized C_n cage between the inner and outer wall of the C_n, and $\alpha < 1$ if only partial shielding of the A^+'s potential occurs. Finally, when solving the corresponding HF equations for the final-state wavefunctions $\psi_f(\mathbf{r})$ of the outgoing photoelectron, the latter are orthogonalized to the ground-state wavefunctions $\psi_i(\mathbf{r})$ with using Lagrange's off-diagonal parameters λ_{ij} in the exactly same manner as for an isolated atom [13]. This corrects for the use of different potentials in the ground-state and final-state HF calculations. The thus defined electronic energies and wavefunctions are starting points for the random phase approximation with exchange (RPAE) equation [13] which allows one to calculate photoionization matrix elements, their phase shifts, and total and differential photoionization cross sections of the $A@C_n$ atom.

To begin with, the direct part of the potential $\mathcal{V}_{nl-\epsilon l'}^{dir}(r)$ of the final-state Hamiltonian $\hat{\mathcal{H}}_c$ seen by an

outgoing $\epsilon l'$ photoelectron due to the photoionization of $A@C_n$ is given by

$$\mathcal{V}_{nl \to \epsilon l'}^{dir} = V_{nl \to \epsilon l'}^{dir}(r) + \frac{l'(l'+1)}{2r^2} + U_c(r) - \frac{\alpha}{r}. \quad (4)$$

Here, $V_{nl \to \epsilon l'}^{dir}(r)$ is a direct atomic Hartree-Fock potential with the excluded centrifugal potential. Note, the atomic exchange potential can be safely ignored at the C_n boundary since the radius of C_n considerably exceeds the atomic size. As an example, the calculated $\mathcal{V}_{nl \to \epsilon l'}^{dir}$ potentials seen by the ϵs and ϵd photoelectron waves upon the $2p$ photoionization of $Ne@C_{60}$ are shown in Fig. 1. One can see that the shielding effect noticeably reduces

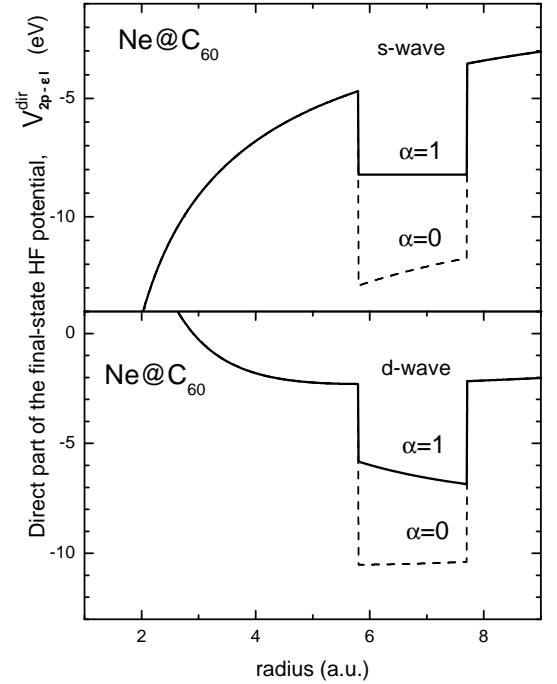FIG. 1: $\mathcal{V}_{nl \to \epsilon l'}^{dir}(r)$ potential seen by the ϵs and ϵd photoelectron waves upon the $2p$ photoionization of $Ne@C_{60}$ calculated both with ($\alpha = 1$) and without ($\alpha = 0$) accounting for a complete shielding of the direct atomic potential of Ne^+ by the static potential of the polarized C_{60}, as discussed in the body of the paper.

the potential depth of $\mathcal{V}_{nl \to \epsilon l'}^{dir}$ inside the C_{60}. Thus, one might expect a noticeable decrease in the confinement resonances, since the coefficient of reflection of the outgoing photoelectron wave by the potential well lessens with decreasing depth of the well.

To illustrate the actual changes in the strengths of confinement resonances, the RPAE calculated $1s$ and $2p$ photoionization cross sections $[\sigma_{1s}(\omega)$ and $\sigma_{2p}(\omega)$, respectively] of $Ne@C_{60}$ versus the photon energy ω for various values of the shielding parameter α are depicted in Fig. 2. One can see that even complete shielding ($\alpha = 1$) results in a no more than a 20% change in the photoionization cross sections near threshold (compared to a "non-shielded" result, $\alpha = 0$), and much less at higher photon
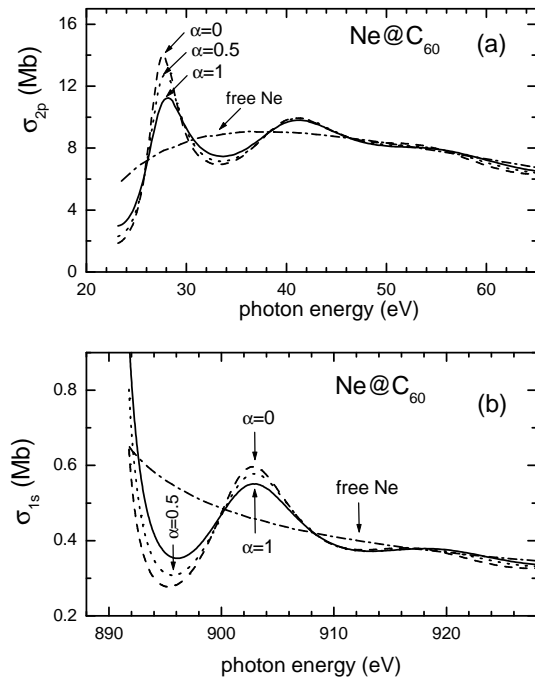
FIG. 2: RPAE calculations of the photoionization cross sections $\sigma_{1s}(\omega)$ and $\sigma_{2p}(\omega)$ of confined Ne (Ne@C$_{60}$) and free Ne, as marked. Dashed line, calculations without accounting for shielding of the direct atomic potential of Ne$^+$ by the static potential of the polarized C$_{60}$ ($\alpha = 0$). Dotted line, calculations accounting for only partial shielding ($\alpha = 0.5$). Solid line, calculations accounting for complete shielding ($\alpha = 1$).

energies. Note, the value of the parameter α for actual shielding is, obviously, somewhere between the extreme values of $\alpha = 0$ and $\alpha = 1$. Hence, the actual impact of the shielding effect on photoionization cross sections is yet smaller than 20% (cf., e.g., results for $\alpha = 0.5$). One can thus conclude that the shielding effect is relatively insignificant for $A@C_n$ photoionization. Thus, it can safely be excluded as a possible factor for "washing out" confinement resonances from the photoionization spectrum of $A@C_n$.

Then, what could be possible reasons for the absence of confinement resonances in the experimental $4d$ photoabsorption spectrum of Ce@C$_{82}^+$? Some reasons for this, like the off-center position and thermal vibrations of the confined ion, were proposed in Refs. [4, 12]. However, we believe that the primary reason for the absence of confinement resonances in the Ce@C$_{82}^+$ spectrum is of a different nature. First of all, the expectations of seeing strong resonances in the Ce@C$_{82}^+$ spectrum were based on the predictions made for the Xe $4d$ absorption spectrum of Xe@C$_{60}$ in Ref. [11] where the "delta"-potential model was used for the description of photoionization of $A@C_{60}$ atoms. In this modeling, the C$_{60}$ cage is modeled by a spherical Dirac bubble potential $U(r) = -A\delta(r - r_0)$, where r_0 is the radius from the center of the C$_{60}$ cage to the middle point between the inner and outer surfaces of the cage, and A is the potential strength. The

δ-potential model thus assumes that the C$_{60}$ cage has a zero thickness, $\Delta = 0$. The predicted confinement resonances on the basis of this model, including confinement resonances in the Xe $4d$ photoionization of Xe@C$_{60}$, are huge. It is not surprising that researchers were expecting the same strong resonances to occur in the $4d$ photoabsorption spectrum of confined Ce as well. However, as was demonstrated in Ref. [14], and for a number of other examples in Ref. [2], accounting for a finite thickness Δ of the C$_{60}$ cage lessens the strength of confinement resonances considerably. This is illustrated in Fig. 3 where the "delta"-potential model calculated results for the $4d$ photoionization of Xe@C$_{60}$ [11] are compared with those [14] obtained in the finite-C$_{60}$-thickness potential model [Eqs. (1) and (2)].
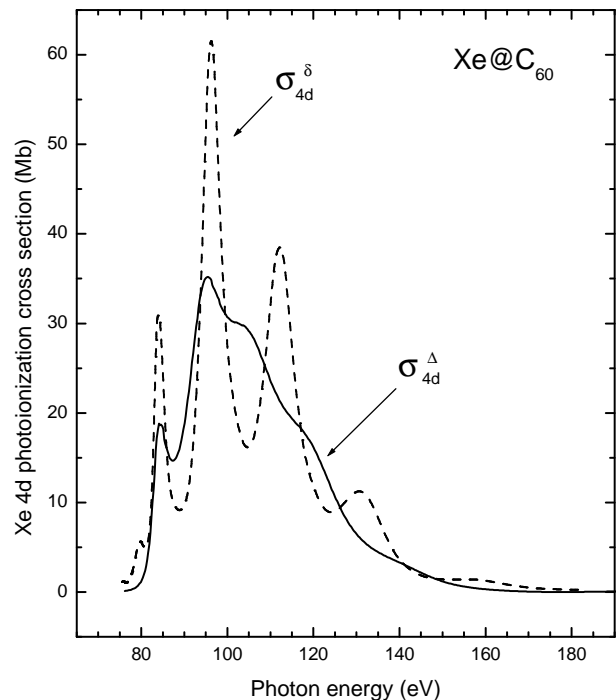

FIG. 3: RPAE results for the $4d$ photoionization cross of confined Xe (Xe@C$_{60}$) calculated within the framework of both the zero-thickness δ-potential model, σ_{4d}^δ [11], and accounting for the finite-thickness Δ of C$_{60}$, σ_{4d}^Δ [14]. The spikes in the cross section are confinement resonances.

One can see that accounting for finite thickness Δ dramatically reduces the confinement resonances in the $4d$ spectrum of Xe@C$_{60}$. We believe that the same is true for the $4d$ spectrum of Ce@C$_{82}^+$ as well. Such weak resonances are probably not observable yet experimentally, owing to the difficulty of performing experiments with such a small number of molecules as are currently available.

In conclusion, it is shown that the possible effects of shielding of the A^+'s field, owing to the polarization of confining shell, are quite weak and, thus, can not lead to the disappearance of the confinement resonances from the spectrum of an endohedral atom $A@C_n$. As for the con-

finement resonances in the $4d$ spectrum of Ce@C$_{82}^+$, it is argued (on the basis of an analogy with the $4d$ spectrum of Xe@C$_{60}$) that they must be quite weak due to the finite-thickness effect. Additionally, the off-the-center-position and thermal vibrations effects further suppress the strength of the resonances. Hence, the combination of the finite-thickness, off-the-center position, and thermal vibrations effects make the confinement resonances in the Ce@C$_{82}^+$ spectrum so insignificant that they, while being there in principle, are not observable experimentally, contrary to expectations based on a zero-thickness model of the C$_{60}$ potential, a model that seems to be quantitatively inaccurate in this situation. These considerations explain the absence of confinement resonances in the measured $4d$ spectrum of Ce@C$_{82}^+$. In other situations, particularly for at-the-center confined atoms, the confinement resonances are likely strong and observable, e.g., see Fig. 2 for the $1s$ and $2p$ near threshold photoionization of Ne@C$_{60}$. We suggest the latter as a test case for experimental study.

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